New Materials & New Techniques for Imaging of Long Wavelength IR Radiation

Final Report

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Cardinal advantages for the pyro-optic reflectance method are:

The thermally sensitive film need only be thick enough to support the evanescent wave on reflection, so that pixel volume (mass) can be exceedingly small.

Films can be mounted upon a critically dehydrated gel substrate which is transparent to visible light but affords near perfect thermal isolation.

There is no need for contacts to individual pixel elements as in the pyroelectric imagers.

Calculations show that for a film 0.1μ meter thick, mounted on a silica gel substrate the thermal efficiency is such that if the thermometric sensitivity of the film is sufficient to detect a temperature change of 1mK then for a system with f(1) optics this could correspond to a temperature difference in the object plane of 0.1K.

The studies on this program were in two parts, the first objective was to verify the high values of temperature derivative of refractive index which had been reported in bismuth vanadate $BiVO_4$, molybdenum disulphide MoS_2 and antimony sulphur iodide SbSI. Here, wavelength scanning ellipsometry was used to examine the spectral response and to chose the monochromatic wavelength of maximum sensitivity. The second objective was to design and build a compact thermoelectric heater cooler which could be used to impart a known small AC temperature change to explore the detectivity limit for a pyro-optic reflectance system.

The experimental measurements using ellipsometry confirmed the literature values for the very high temperature derivatives of refractive index in the candidate crystals and suggested that SbSI would be the best crystal for the pyro-optic application.

Using the temperature modulator at a frequency of 3.7Hz it was possible using SbSI to detect temperature variations of 0.02K, the lowest possible with the AC source and to show a signal to noise ratio of 25 at this level. With MoS_2 in a less perfect film form, it was possible to detect 0.03K but the signal to noise ratio was inferior to SbSI.

Optical studies on the MoS_2 and the SbSI have been submitted for publication and the papers are included on Appendix I and Appendix II. These studies were also presented at the American Ceramic Society National Meeting in Dallas, May 1990 and at the International Symposium on Applications of Ferroelectrics in Urbana, Illinois in June 1990.

The topic appeared so promising that the University has applied for patent on this method of imaging and the patent documentation is included as Appendix III.

From the present studies it does appear feasible to construct a rather simple pyro-optic detector of very high sensitivity using SbSI and a proposal for continuation of this work is appended.

ABSTRACT

Work on this program was directed towards the preliminary verification of the possibility of a completely new type of long wavelength infra-red imaging system. In the past many IR imaging methods have been proposed which purport to use the change of refractive index of a solid (liquid) induced by local temperature charge associated with the absorption of long wavelength IR radiation. These pyro-optic systems used transmission through the medium to modify the optical (visible light) path length, and all suffer heavily in thermal sensitivity because of the volume (mass) of the optical material which must be heated. In this study it was proposed to explore the change in polarized reflectance from the pyro-optic surface making use of the exceptional sensitivity of the newer ellipsometric techniques for reflectance studies.

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Using the temperature modulator at a frequency of 3.7Hz it was possible using SbSI to detect temperature variations of 0.02K, the lowest possible with the AC source and to show a signal to noise ratio of 25 at this level. With MoS_2 in a less perfect film form, it was possible to detect 0.03K but the signal to noise ratio was inferior to SbSI.

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INTRODUCTION

The purpose of this initiative program was to identify and study materials which could be used in a pyro-optic IR imaging device. This device would operate on the measurement of the temperature by monitoring the change in the reflectance coefficient. The leading figure of merit for a candidate material would be a high temperature derivative of the refractive index. A list of the initial candidates is given in Table 1 along with the temperature derivative of the coefficient and respective operational temperature range. $BiVO_4$, MoS_2, and SbSI were chosen as the candidates with the most promise for applications in this contract.

The study was broken into two parts. The first was the verification of a high temperature derivative of the refractive index for the materials of interest using spectroscopic ellipsometry. The wavelength and temperature range of optimum operation were then identified. The second part was to measure the sensitivity of the reflectance coefficient to a small AC temperature modulation using null ellipsometry. This measurement allowed for the determination of the smallest temperature change which could be detected. The conditions for optimum sensitivity were then evaluated. MoS_2 and SbSI were found to be the two best candidates. Their temperature derivatives were found to be 0.01 and 0.001 $^{o}C^{-1}$, respectively. It was then found that a temperature change of 0.001^{o}C could

feasibly be detected by monitoring the reflectance coefficient of SbSI using null ellipsometry.

LITERATURE REVIEW

$BiVO_4$

Bismuth Vanadate ($BiVO_4$) is a ferroelastic material in the Aizu class 4/mF2/m(2). $BiVO_4$ has a transition temperature near 528°K. At the phase transformation, the Bi and V atoms distort along the c axis. The birefringence, Δn, of $BiVO_4$ is large and decreases continuously with increasing temperature especially near T_c where Δn changes rapidly.

MoS_2

Molybdenium disulphide (MoS_2) belongs to the group VIA transition metal dichalcogenides. MoS_2 is a semiconductor with a layer structure whose physical properties are known to be strongly anisotropic. The bonding in a layer is covalent, and the interlayer bonding is VanDerWals in nature. Two polymorphic forms of MoS_2 are known to exist (2H,3R) which differ only in the way the layers are stacked. The optical properties of single crystalline 2H-MoS_2 have been studied previously by Khan and Goldsmith. At temperature 85°K, they found two major peaks at 1.916 and 2.128 eV using wavelength modulated reflectivity spectrum which were clearly related to prominent peaks in the reflectivity spectrum. These two peaks shifted with temperature, and were believed to be arise from the ground states of two different excitons. Four minor peaks in the modulation spectrum were also found

between 1.916 and 2.128 eV which were believed to be higher states of the excitons.

SbSI

Antimony sulfur iodide (SbSI) is a ferroelectric semiconductor in the Aizu class mmmFmm2(2). SbSI has a transition temperature near 20^{o}C. Only 180^{o} domains are allowable with the polar axis along the c direction. The optical properties of SbSI are known to be strongly coupled to its polar nature, and the presence of a relatively high concentration of nonequilbrium electrons near the phase transition temperature. SbSI has a relatively high refractive index which is strongly temperature dependent. A strong electric field dependence of the absorption edge has been reported. The ferroelectric transition temperature has also been reported to be strongly dependent on illumination with light.

EXPERIMENTAL PROCEDURE

PART I

The wavelength of the maximum temperature derivative of the refractive index of $BiVO_4$, MoS_2, and SbSI was determined by using spectroscopic ellipsometry in this section. The experimental apparatus is shown in Figure 1. The temperature range was from 25 to 120°C. At each fixed temperature, the reflectance coefficient was measured as a function of the wavelength. $\Delta n/\Delta T$ was calculated, and then averaged to improved the precision. By plotting $\Delta n/\Delta T$ against the photon energy, the wavelength of maximum sensitivity was determined.

PART II

The temperature sensitivity of the reflectance coefficients of SbSI and MoS_2 were measured using a null ellipsometer with a thermoelectric sample mount in this section. The experimental setup is shown in Figure 2. A function generator supplied a signal to a power amplifier which subsequently powered the thermoelectric element. A DC signal was used to set the base temperature and the AC signal was superimposed to give the temperature variation. The SbSI and MoS_2 samples were mounted directly on the thermoelectric element with a heat sink compound. The change in the reflectance coefficient with the temperature modulation by converting the output

current from the photomultiplier tube to a voltage and then phase locking to the temperature change with a lock-in amplifier. A signal was taken from the output of the lock-in amplifier to an oscilloscope for direct reading. Small temperature changes of about 0.02^{o}C were detected at 2.7 and 3.7 Hz.

SAMPLE INFORMATION

$BiVO_4$: The sample was a single crystal orientated along the (100) direction. Measurements were made with the a axis perpendicular to the surface of the sample with an incidence angle of 70^{o}.

MoS_2: The sample was a natural single crystal obtained from the National Museum of Natural History (catalogue number NMNH 126914). The crystal was cleaved using cellulose tape to remove successive layers until a desired thickness was obtained. The sample was optically flat at local regions. The beam size was relatively small in comparison to the surface, so it was assumed that the sample was optically flat throughout a measurement sweep. All measurements for MoS_2 were made with the c axis perpendicular to the sample surface with an incidence angle of 70^{o}.

SbSI: The sample was a single crystal of dimensions $3x2x1mm^3$ and was grown by a modified Bridgeman technique. The measurements on SbSI were made with the c axis in the incidence plane at an incidence angle of 70^o.

RESULTS AND DISCUSSION

PART I:

Figure 3 shows the refractive index versus the wavelength at various temperatures for $BiVO_4$. Figure 4 shows the temperature derivative versus the wavelength as calculated from the data shown in Figure 3. At a photon energy near 2.0 ev, $\Delta n/\Delta T$ reached a maximum indicating that the maximum temperature sensitivity was near this wavelength.

The refractive index of MoS_2 at various temperatures and its temperature derivative are shown as functions of wavelength in Figures 5 and 6, respectively. The refractive index had maximums at 1.80, 2.00, and 2.50 eV as shown in Figure 5. The peaks at 1.80 and 2.00 eV shifted to lower energies and broadened slightly with increasing temperature. The magnitude of the $\Delta n/\Delta T$ was approximately 10^{-2} at 1.84 eV and 0.5x 10^{-2} at 2.02 eV as shown in Figure 6. A wavelength of 2.02 eV was then chosen for the temperature sensitivity study of Part II.

The room temperature refractive index and absorption coefficient as a function of wavelength for SbSI are shown in Figure 7. The refractive index decreased dramatically between 2.04 and 3.50 ev with a maximum value of 3.7 near 2.04 ev (absorption edge), at lower photon energies it slowly decreased. From this data photon energy near 2.04 ev was selected for the

temperature sensitivity study in Part II because of the large refractive index and approximity to the absorption edge.

PART II:

Figure 8 shows the dependence of the 613 nm (2.02 ev) reflectance coefficient of MoS_2 at 32°C on the magnitude of the temperature modulation. A linear dependence was found between 0.03 and 0.11°C. Figure 9(a) and (b) show the 613 nm reflectance coefficient response and the corresponding temperature modulation, respectively. It is obvious from Figure 9(a) that the reflectance coefficient is sensitive to significantly smaller temperature variations than 0.03°C. The signal to noise ratio was four using a temperature modulation of 0.03°C. This indicates that a temperature change of less than 0.01°C can be measured using the pyro-optic properties of MoS_2. From Figure 5 which shows a consistent shift with temperature in the energy of the refractive index peak above room temperature and from the work of Khan and Goldsmith who found a similar shift between -123 and 0°C, the reflectance coefficient of MoS_2 can be expected to be sensitive to small temperature changes over a very large temperature interval (-100 to 100°C).

Figure 10 shows the change of the 633 (1.96) and 580 nm (2.14 ev) reflectance coefficients of SbSI with temperature modulation. The base temperature was between 5 and 35°C with a 3.7 Hz AC modulation of approximately 0.02°C. A sharp maximum in the change of the 633 nm reflectance coefficient

was observed at 18.4°C which is close to the transition temperature of SbSI. Similar results were obtained for the 580 nm reflectance coefficient, but the curve was shifted to higher temperature. This shift in the reflectance data is due to a coupling of the spontaneous polarization to the density of non-equilibrium electrons near the transition temperature. The phase transition in a ferroelectric semiconductor is accompanied by anomalies in the temperature dependence of the carrier concentration due to a change in the donor activation energy and the effective mass of the carriers. For wavelengths smaller than 580 and larger than 680 nm the temperature sensitivity of the reflectance coefficient was significantly smaller. Only in the wavelength region of the absorption edge was the temperature sensitivity large. The maximum sensitivity of photoconduction for a single crystal of SbSI was between 630-640 nm. The width of the peak depends on the experimental conditions.

Figure 11 shows the dependence of the 580 nm reflectance coefficient on the magnitude of the temperature modulation at 14.7°C. A linear dependence was found between 0.02 and 0.07°C. Figures 12 (a) and (c) show the 580 nm reflectance coefficient response and the corresponding temperature modulation of 0.02°C, respectively. Figures 12 (b) and (d) show the same parameters, respectively, but with no temperature modulation. Figures 12 (e) shows the same results as (b), but the sensitivity of the lock-in amplifier was increased by a factor of 25. The amplitude of the noise in Figure 12 (e) was

approximately of the same amplitude as that of Figure 12 (a). It was concluded that signal to noise ratio was approximately 25:1 using a temperature modulation of 0.02°C. This extrapolation indicates that a temperature change of 10^{-3} °C can be detected using the pyro-optic properties of SbSI. Further increases in the sensitivity, i.e. detection of a ΔT smaller than 10^{-3} °C, may be achieved using thinner samples or thin films.

SUMMARY

A new type of long wavelength IR imaging system has been proposed in which the thermal change in a thin film absorbing element is detected as a modulation of the visible light reflectance from the film. The dominant figure of merit of the material used in this application would be the temperature derivative of the refractive index. A high $\Delta n/\Delta T$ in $BiVO_4$, MoS_2 and SbSI have been confirmed. The magnitude of $\Delta n/\Delta T$ in these three materials was found to be suitable for pyro-optic applications. The wavelength of the maximum sensitivity for these three materials has been identified using wavelength scanning ellipsometry. A thermoelectric sample mount was then fabricated which could control an AC temperature modulation of 10^{-2} °C at 4 Hz. The change of the reflectance coefficient was then monitored as a function of the temperature modulation. In SbSI an extrapolated response shows the potential to detect a temperature change of 10^{-3} °C in an as yet unoptimized system.

The detection of a temperature change of 10^{-3} °C at the image scene translates to 10^{-1} °C at the object scene. This is superior to the best thermal imagers. There would be several potential advantages of this proposed device over current thermal imagers. First, there would be an elimination of electrical contact to each pixel element. Secondly, the operational speed would be faster meaning higher resolution

and greater sensitivity. And finally, there are possibilities for a vastly improved thermal design superior to the best pyroelectric point detectors.

FUTURE WORK

1) Further optimization of the operational parameters needs to be done. These include system noise, sample thickness, surface quality, incidence angle, etc.

2) Effect on the sensitivity of the reflectance coefficient by an electric field.

3) Develop thin films of SbSI on glass. This will minimize effects of thermal conductivity.

4) Determine the minimum pixel size which is feasible, and to use a fiber optics interogating beam.

5) Develop an operational low level light VIDICON.

Table 1. Some protenal material for optical infrared sensing devices

Material	Temperature range (°C)	$\frac{\delta(\Delta n)}{\delta T}$ (/°C)
$BiVO_4$	20°C to 100°C	2.8 $\times 10^{-4}$
MoS_2	20°C to 50°C	$dn/dT = 163 \times 10^{-4}$
SbSI	0°C to 15°C	$dn_c/dT = 7.5 \times 10^{-3}$
$PbTiO_3$	-60°C to -40°C -60°C to 0°C	1.5 $\times 10^{-4}$ 1.6 $\times 10^{-4}$ (λ=5150Å)
$BaTiO_3$	20°C to 120°C	3.1 $\times 10^{-4}$
DSP	-40°C to 0°C	2.5 $\times 10^{-5}$
Fe -I Boracite	25°C to 70°C	3.3 $\times 10^{-5}$
Cu-Cl Boracite	80°C to 90°C	4.0 $\times 10^{-5}$
TGS	40°C to 300°C	3.3 $\times 10^{-5}$
SBN (61:39)	20°C to 80°C	4.5 $\times 10^{-4}$
PBZT	120°C to 130°C	5.0 $\times 10^{-4}$

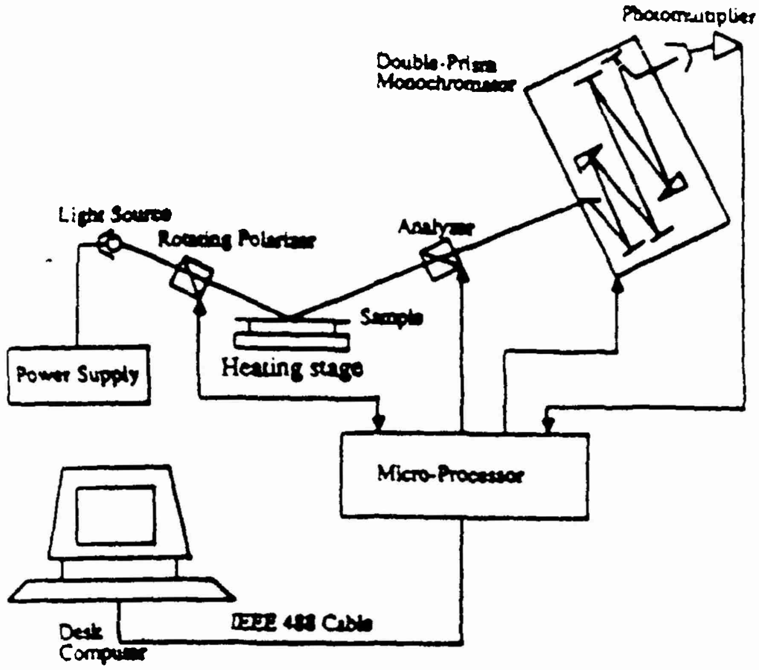

Figure 1. A schematic representation of automated spectroscopic ellipsometer

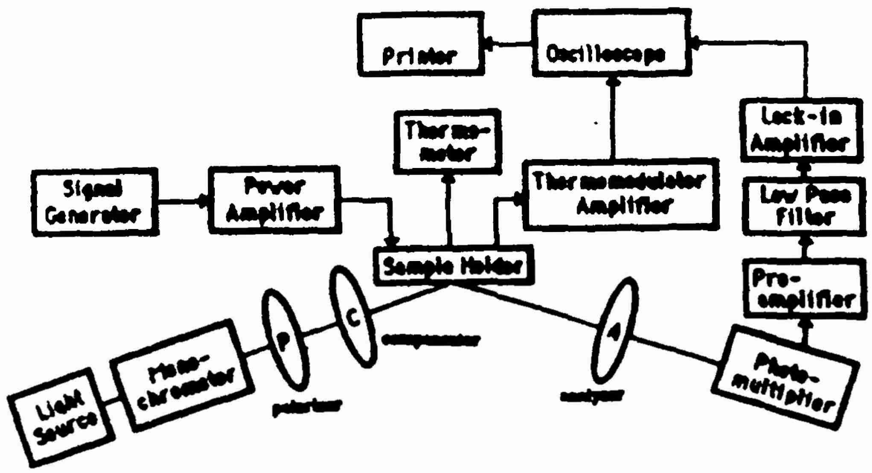

Figure 2. Schematic drawing of the exprimental equipment set up. P: polarizer, C: compensator, A: analyzer.

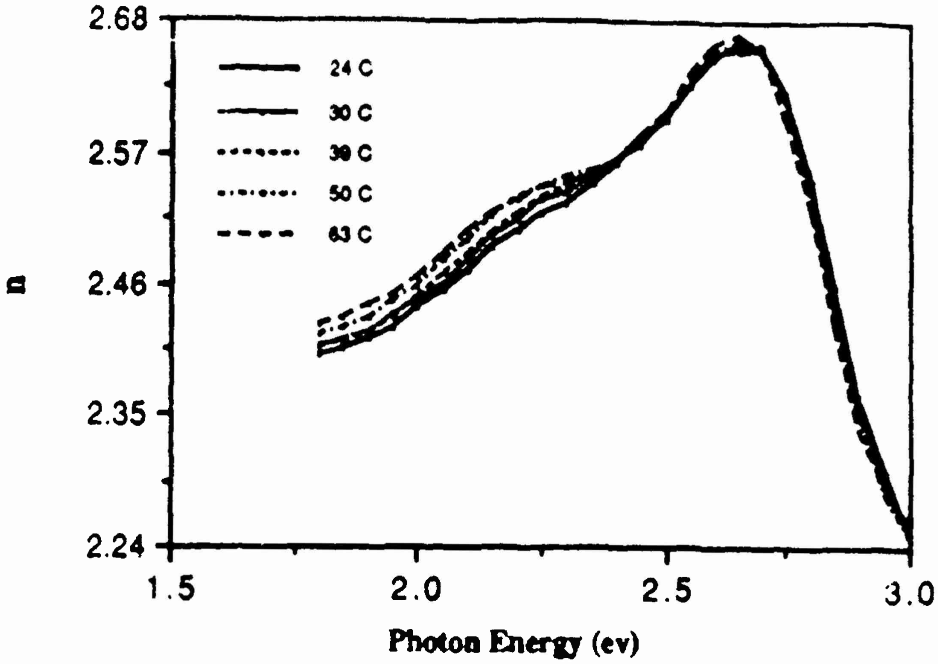

Figure 3. Plot of the refractive index (n) of $BiVO_4$ as a function of photon energy at 24,30,39,50 and 63 °C.

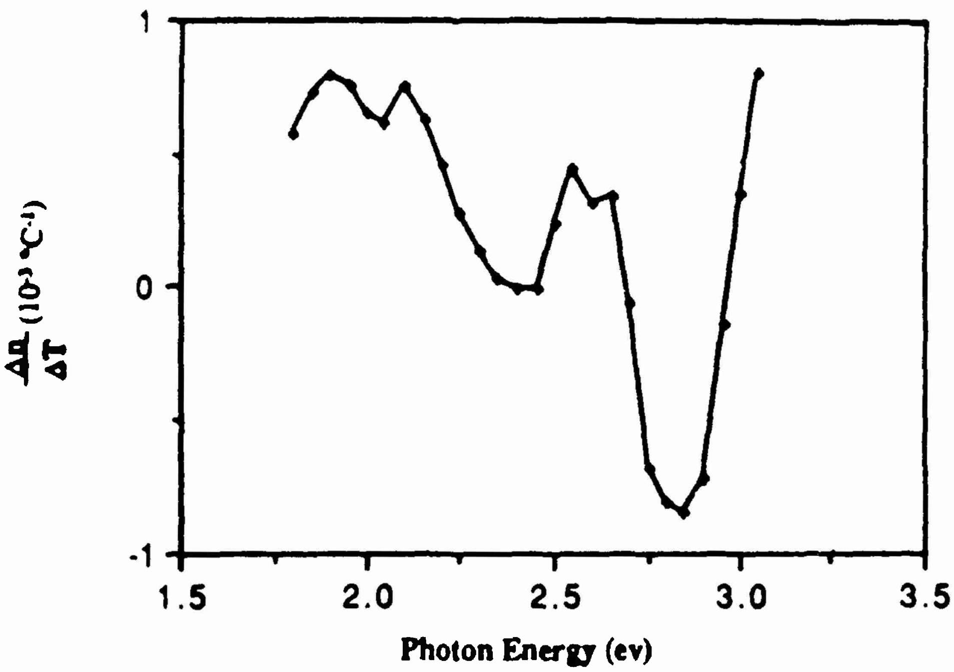

Figure 4. Plot of the temperature derivative of the refractive index (n) of $BiVO_4$ as a function of photon energy.

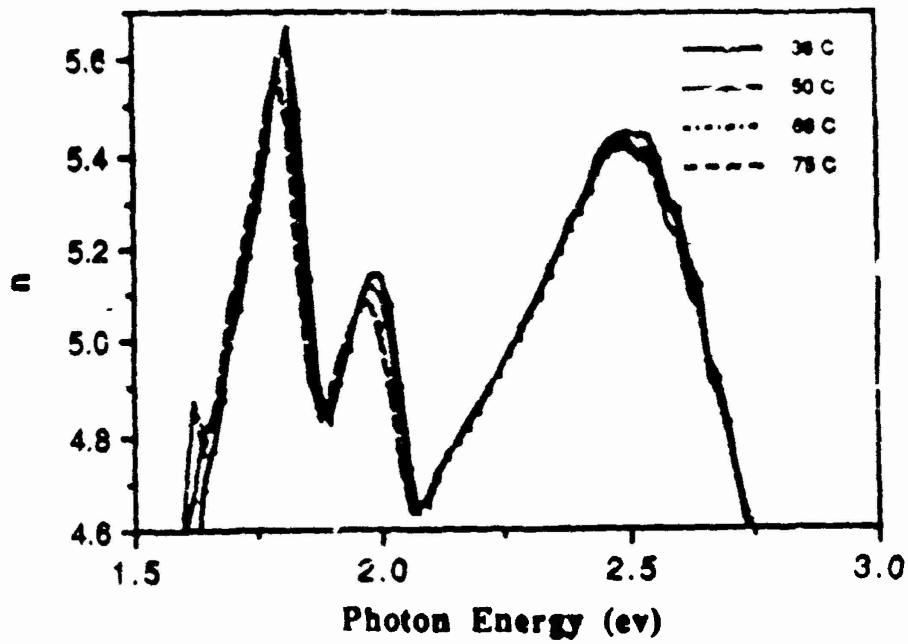

Figure 5. Plot of the refractive index (n) of MoS_2 as a function of photon energy at 36, 50, 66, 75 °C.

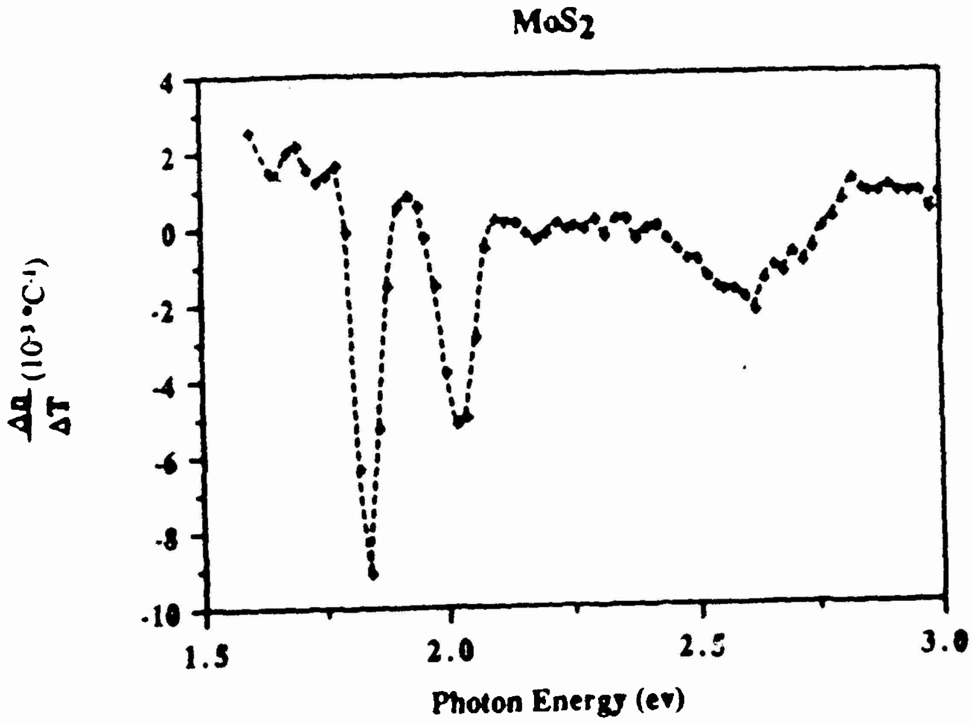

Figure 6. Plot of the temperature derivative of the refractive index (n) of MoS_2 as a function of photon energy.

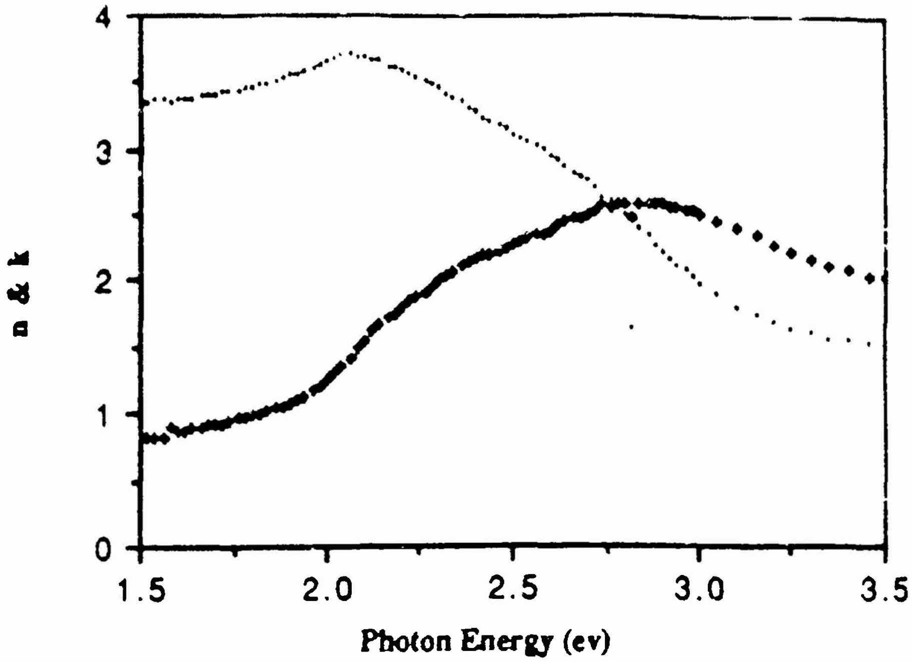

Figure 7. Refractive index (n) and absorption coefficient (k) of SbSI single crystal at room temperature as a function of photon energy.

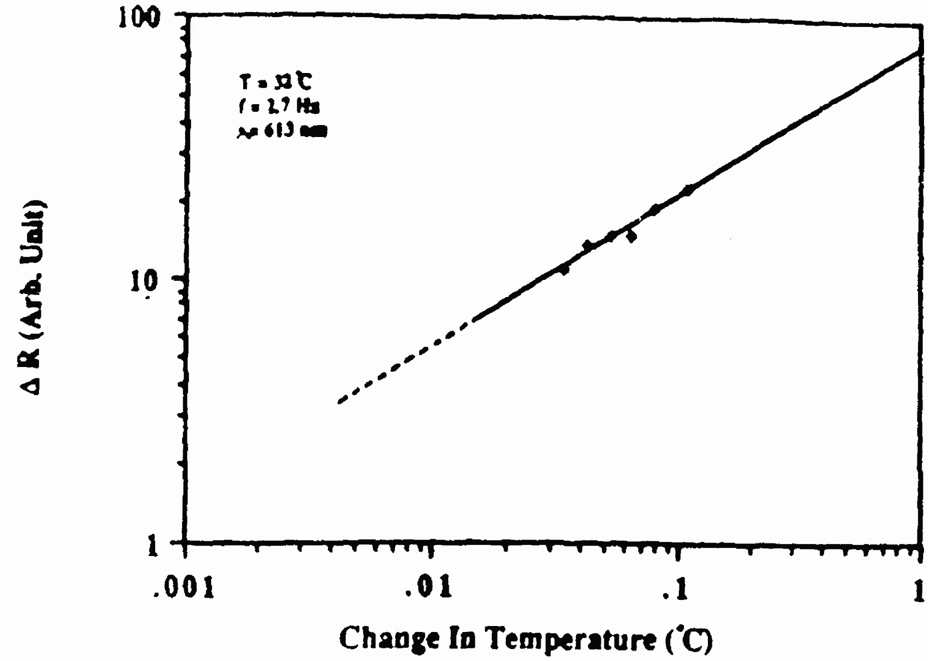

Figure 8. The dependence of the changing reflectance coefficient on the amplitude of the ac temperature modulation, at a base temperature of 32 °C, a photon energy 2.02 eV, and a frequency of 2.7 Hz.

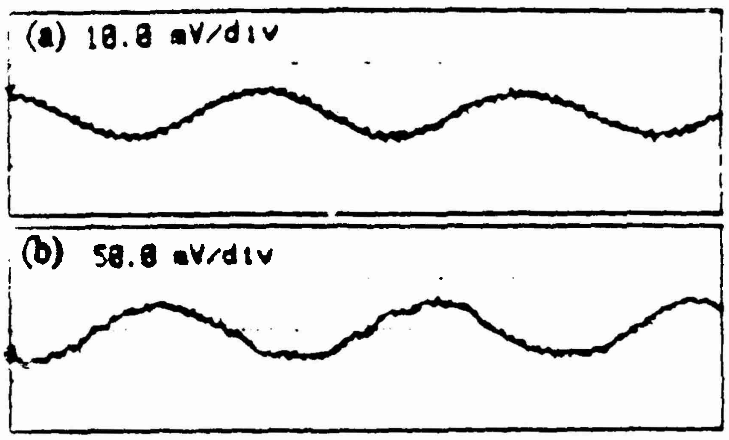

Figure 9. (a) Modulation of the reflectance coeffocient under a 2.7 Hz temperature modulation of 0.03 °C. (b) The temperature modulation.

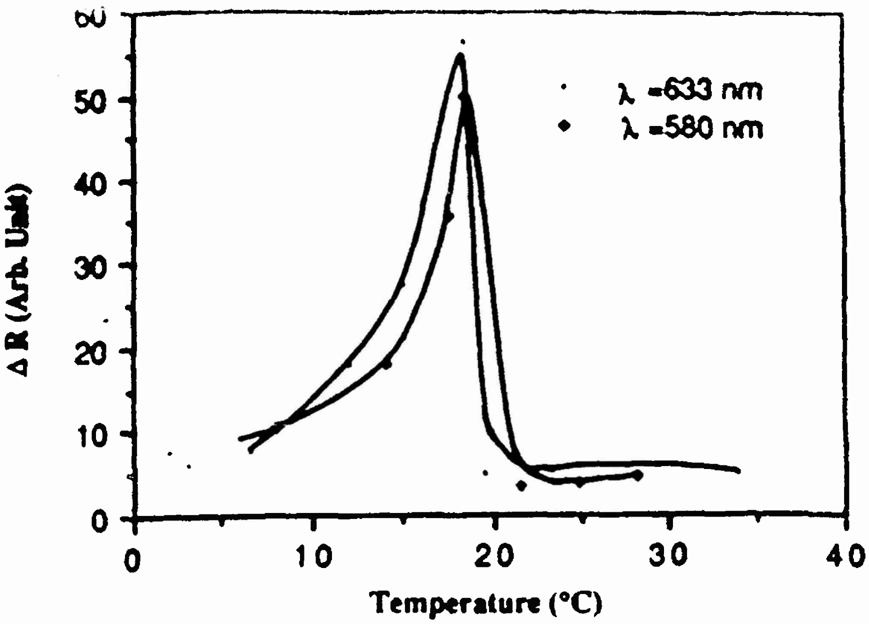

Figure 10. The change in the reflectance coefficient under a 3.7 Hz temperature modulation of 0.02 °C as a function of the base temperature.

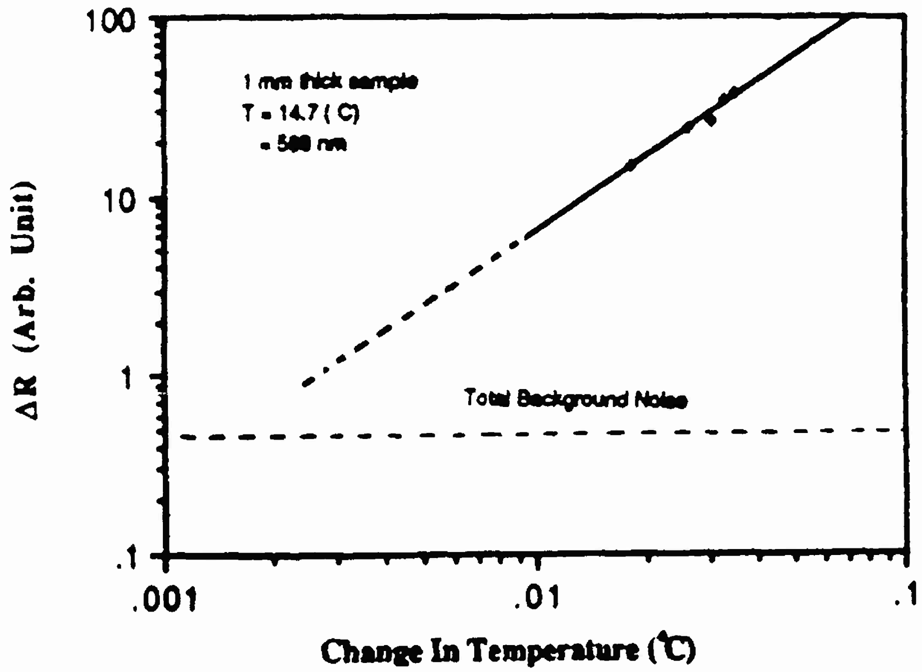

Figure 11. The dependence of the changing reflectance coefficient on the amplitude of the ac temperature modulation, at a base temperature of 14.7°C, a wavelength of 580 nm, and a frequency of 3.7 Hz.

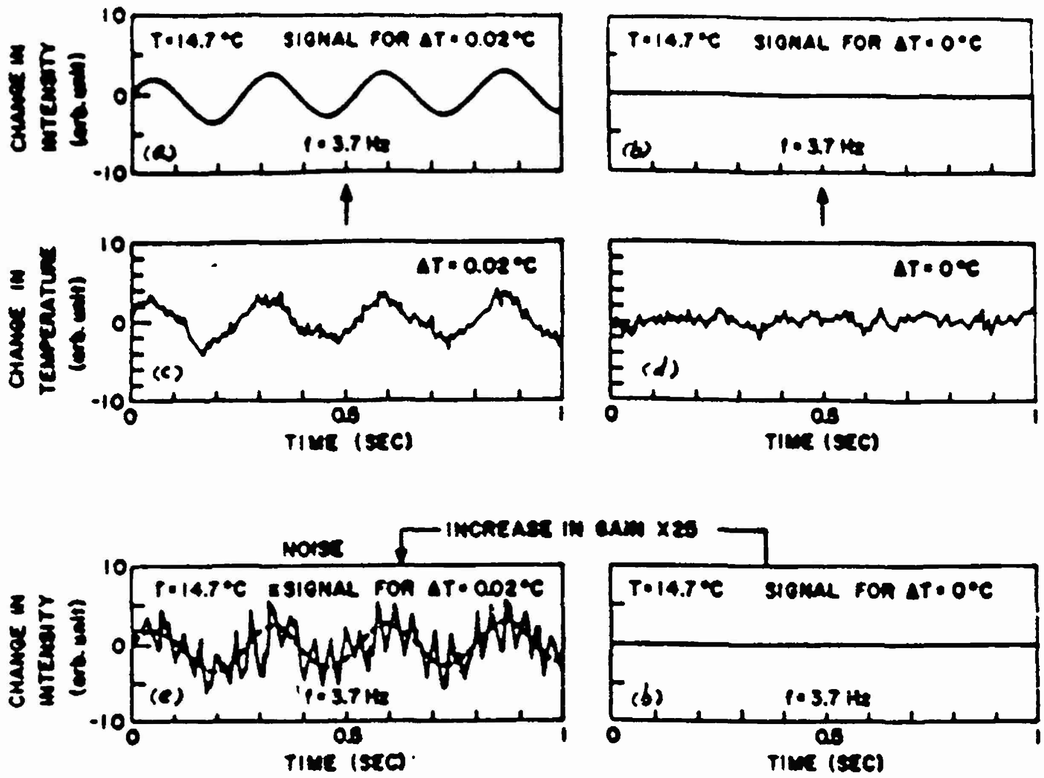

Figure 12. (a) and (b) Modulation of the reflectance coeffocient under a 3.7 Hz temperature modulation of 0.02 ^{o}C and 0 ^{o}C. (c) and (d) The temperature modulation. (e) Signal for ΔT=0, but increase in gain x 25.

Papers Presented at the Meetings:

1. "Pyro-Optic Properties of SbSI & $BiVO_3$," American Ceramic Society Meeting (1989).

2. "Temperature Sensitivity of the Refractive Indices of MoS_2, $BiVO_3$ & SbSI for Pyro-Optic Applications," The VII International Symposium in Application of Ferroelectrics," Urbana, Illinois (June 1990).

Papers Submitted for Publication:

1. "Temperature Dependence of the Optical Constants of MoS2 for Pyro-Optical Devices," J.F. Li, A.S. Bhalla, D. Damjanovic, K. Vedam, L.E. Cross and F.W. Ainger, Submitted. (Appendix 1)

2. "Temperature Sensitivity of the Reflectance Coefficient of SbSI," J.F. Li, A.S. Bhalla and L.E. Cross, Ferroelectrics Letters. (Appendix 2)

Patent Application.

Pyro-Optic Detector and Imager. L.E. Cross, A.S. Bhalla and D. Damjanovic, F.W. Ainger.

APPENDIX 1

TEMPERATURE DEPENDENCE OF OPTICAL CONSTANTS OF MOS_2 FOR PYRO-OPTICAL DEVICES

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ABSTRACT

The temperature sensitivity of the reflectance coefficient of MoS_2 under small temperature modulations has been investigated. It is feasible to detect temperature changes of 10^{-2} °C by monitoring the reflectance coefficient and thus MoS_2 is a potential candidate material for the pyro-optical sensors.

KEY WORDS/PHRASE

temperature sensitivity   reflectance coefficient   ellipsometry

temperature modulation   pyro-optical sensors

Molybdenium disulphide (MoS_2) belongs to the group VIA transition metal dichalcogenides. MoS_2 is a semiconductor with a layer structure whose physical properties are known to be strongly anisotropic (1,2). The bonding in a layer is covalent, and the interlayer bonding is VanDerWals in nature. Two polymorphic forms of MoS_2 are known to exist (2H,3R) (3,4) which differ only in the way the layers are stacked. The optical properties of single crystalline 2H-MoS_2 have been studied previously by Khan and Goldsmith (5). They found two major peaks in the 85 ^{0}K wavelength modulated reflectivity spectrum at 1.916 and 2.128 eV which were clearly related to prominent peaks in the reflectivity spectrum. These peaks were believed to be the ground states of two different excitons. Four minor peaks in the modulation spectrum were also found between 1.916 and 2.128 eV which were believed to be higher states of the excitons. The position and breadth of the major peaks were found to depend on temperature. As the temperature was increased the peak position shifted to lower energies and broadened, and at high temperature the four minor peaks disappeared. The purpose of this study was to investigate the temperature sensitivity of the refractive index for potential uses in the pyro-optical sensors.

The wavelength of the maximum temperature derivative of the refractive index of MoS_2 was determined by using spectroscopic ellipsometry (6) with a heating stage. The temperature range of the heating stage was from room temperature to about 100^{o}C. At each fixed temperature, the refractive index was measured as a function of the wavelength. $\Delta n/\Delta T$ was calculated, and then averaged to improved the precision. By plotting $\Delta n/\Delta T$ against the photon

energy, the wavelength of maximum sensitivity was determined. The wavelength of a high temperature dependence of the optical constants was identified for an in depth study. The temperature sensitivity of the reflectance coefficient of MoS_2 was measured using a null ellipsometer with a thermoelectric sample mount (7). The MoS_2 sample was mounted directly on the thermoelectric element with a heat sink compound. Small temperature changes of about 0.03 ^oC were achieved at 2.7 Hz.

A single crystal of natural MoS_2 was obtained from the National Museum of Natural History (catalogue number NMNH 126914). The crystal was cleaved using cellolouse tape to remove successive layers until a desired thickness was obtained. The sample was optically flat at local regions throughout the sample. The beam size was relatively small in comparison to the surface, so it was assumed that the sample was optically flat throughout a measurement sweep. All measurements were made with the c axis perpendicular to the plane of surface with an incidence angle 70^o.

The refractive index at various temperatures and the temperature derivative of the refractive index as functions of wavelength are shown in figures 1 and 2, respectively. The coefficients were measured using spectroscopic ellipsometry. The index of refraction had peaks at 1.85, 2.02, and 2.50 eV as shown in figure 1. The peaks at 1.85 and 2.02 eV shifted to lower energies and broadened slightly with increasing temperature in close agreement with Khan and Goldsmith (5). The magnitude of the temperature derivative of the refractive index was approximately 10^{-2} at 1.84 eV and $0.5x10^{-2}$ at 2.02 eV as

shown in figure 2. A wavelength of 2.02 eV was then chosen for a sensitivity study of the refractive index to small amplitude temperature modulations.

Figure 3 shows the dependence of the 2.02 eV reflectance coefficient at 32 ^{o}C on the magnitude of the temperature modulation. A linear dependence was found between 0.03 and 0.11 ^{o}C. Figure 4(a) and 4(b) show the 2.02 eV reflectance coefficient modulation and the corresponding temperature modulation, respectively. It is obvious from figure 4(a) that the reflectance coefficient is sensitive to significantly smaller temperature variations than 0.03 ^{o}C. The signal to noise ratio was four using a temperature modulation of 0.03 ^{o}C. This indicates that a temperature change of less than 0.01 ^{o}C can be measured using the pyro-optic properties of MoS_2. From figure 2 which shows a consistent shift with temperature in the energy of the refractive index peak above room temperature and from the work of Khan and Goldsmith who found a similar shift between -123 and 0 ^{o}C, the refractive index of MoS_2 can be expected to be sensitive to small temperature changes over a very large temperature interval.

The refractive index of MoS_2 was found to be strongly temperature sensitive at a wavelength of 2.02 eV. The reflectance coefficient was able to follow temperature modulations between 0.03 and 0.11 ^{o}C at 2.7 Hz. Considerations of the signal to noise ratio indicate it is feasible to detect temperature changes smaller than 0.01 ^{o}C by monitoring the reflectance coefficient.

ACKNOWLEDGEMENT

The authors would like to extend their gratitude to the National Museum of Natural History for supplying the crystal used in this investigation.

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Figure 1 Plot of the refractive index (n) as a function of photon energy at 36, 50, 66, 75 ^{o}C.

Figure 2. Plot of the temperature derivative of the refractive index as a function of photon energy.

Figure 3. The dependence of the changing reflectance coefficient on the amplitude of the ac temperature modulation, at a base temperature of 32 ^{o}C, a photon energy 2.02 eV, and a frequency of 2.7 Hz.

Figure 4. (a) Modulation of the reflectance coeffocient under a 2.7 Hz temperature modulation of 0.03 ^{o}C. (b) The temperature modulation.

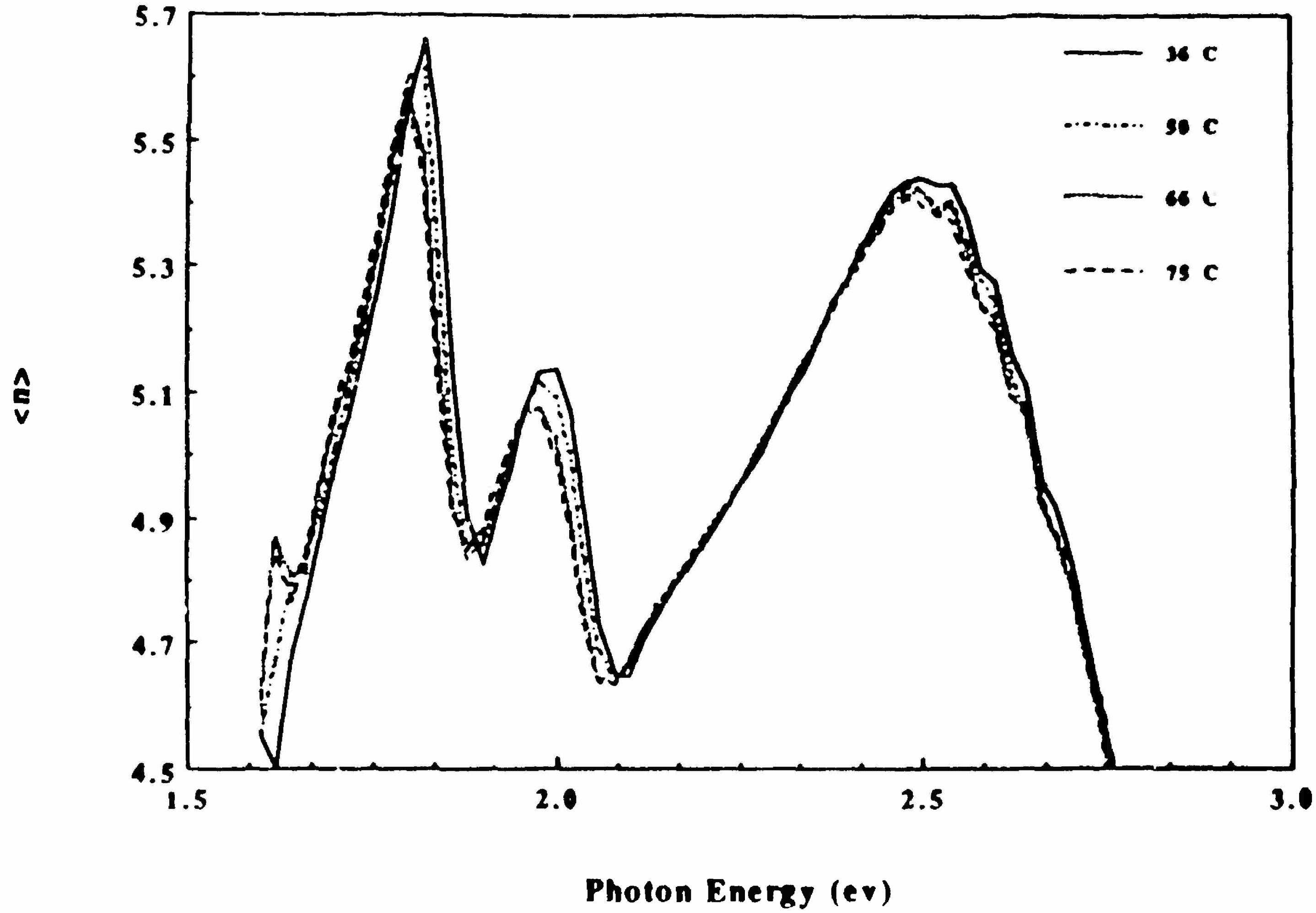
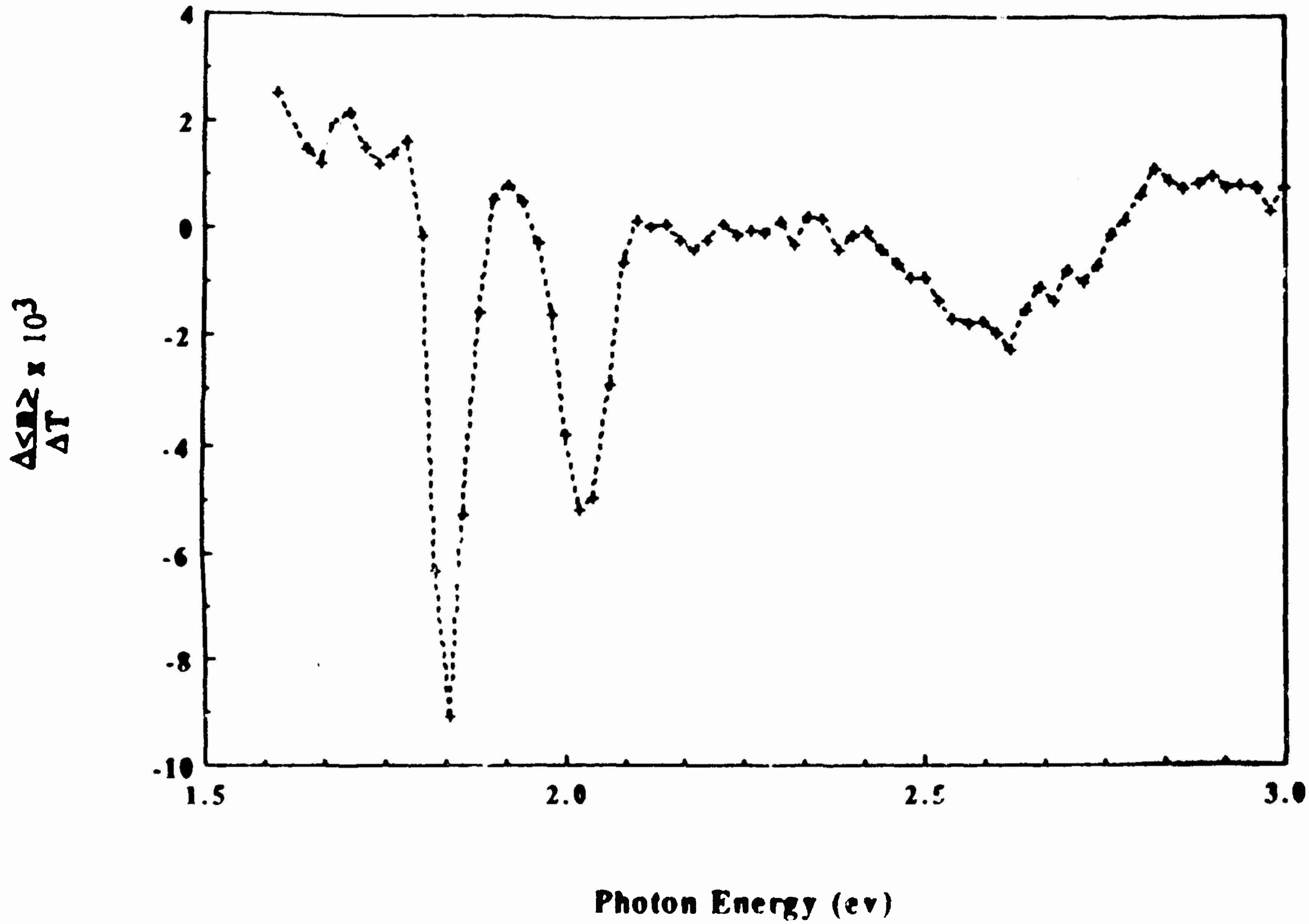


fig. 1 (JFL)



$\frac{\Delta \langle n \rangle}{\Delta T} \times 10^3$
4
2
0
-2
-4
-6
-8
-10
1.5
2.0
2.5
3.0
Photon Energy (ev)

fig 2 (JFC:)

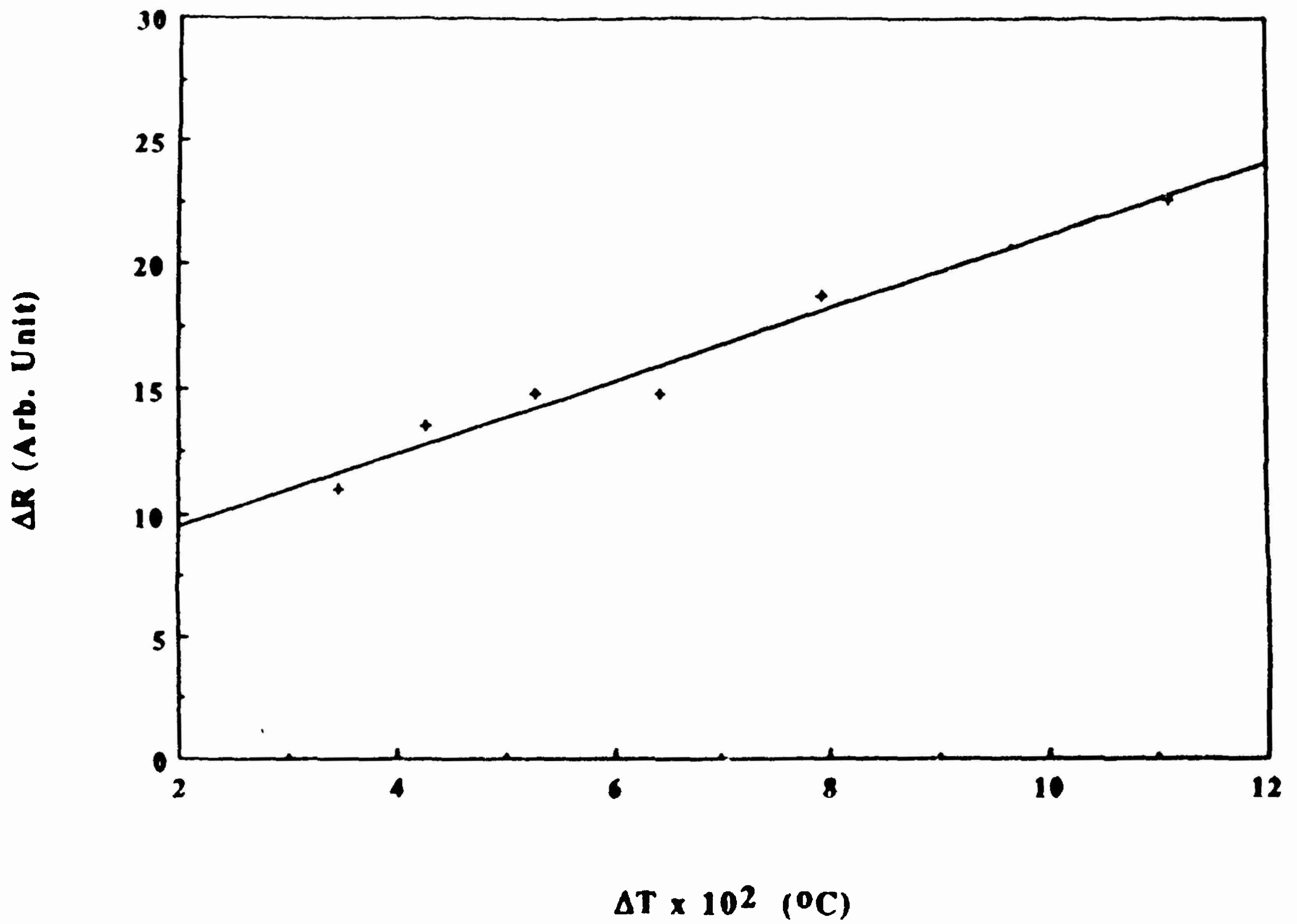
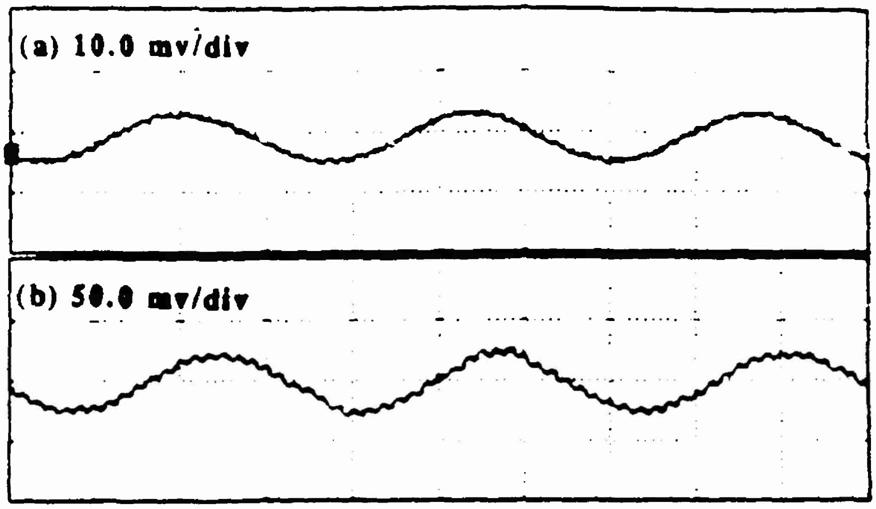


fig 3 (JFL


(a) 10.0 mv/div
(b) 50.0 mv/div

APPENDIX 2

TEMPERATURE SENSITIVITY OF THE REFLECTANCE COEFFICIENT OF SbSI

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ABSTRACT

The reflectance coefficient of SbSI has been studied under a small temperature modulation using null ellipsometry. The intent of this work was to determine the temperature sensitivity of the optical constants. The reflectance coefficient was found to be highly sensitive to small temperature changes at wavelengths around the absorption edge. It is feasible to detect temperature changes of 10^{-3} °C by monitoring the reflectance coefficient.

INTRODUCTION

Antimony sulfur iodide (SbSI) is a ferroelectric semiconductor (1) in the Aizu class mmmFmm2(2) (2). Only 180° domains are allowable with the ferroelectric axis along the c axis below the transition temperature ~ 20 °C. The optical properties of SbSI are known to be strongly coupled to its polar nature, and the presence of a relatively high concentration of non-equilibrium electrons near the phase transition temperature. A strong electric field dependence of the absorption edge has been reported (3,4). The ferroelectric transition temperature has also been reported to be strongly dependent on illumination with light (5). The optical properties have previously been studied by birefringence measurements (6), by polarizability measurements using reflectance ellipsometry (7), by refractive index measurements (8), and by intrinsic optical bistability (5). All of these studies have reported a strong temperature dependence of the optical coefficient in the vicinity of the ferroelectric transition temperature. The purpose of this work was to investigate the sensitivity of the reflectance coefficient to small changes in temperature. Such studies are aimed to explore the new type of temperature sensitive devices.

EXPERIMENTAL PROCEDURE

The temperature sensitivity of the reflectance coefficient of SbSI was measured using a null ellipsometer (9) with a thermoelectric sample mount. The experimental setup is shown in Fig. 1. A function generator supplied a signal to a power amplifier which subsequently powered the thermoelectric element. A dc signal was used to set the base temperature and the ac signal was superimposed to give the temperature variation. The SbSI sample was mounted directly on the thermoelectric element with a heat sink compound. The change in the reflectance coefficient with the temperature modulation was measured by converting the output current from the photomultiplier to a voltage and then phase locking to the temperature change with a lock-in amplifier. A signal was taken from the output of the lock-in amplifier to an oscilloscope for direct reading. Small temperature change of about 0.02 ^{o}C was achieved at 3.7 Hz. The sample was a single crystal of dimensions 3x2x1 mm^3 and was grown by the modified Bridgeman technique (10). All measurements were made with the c axis in the incidence plane with an incidence angle of 70^{o}.

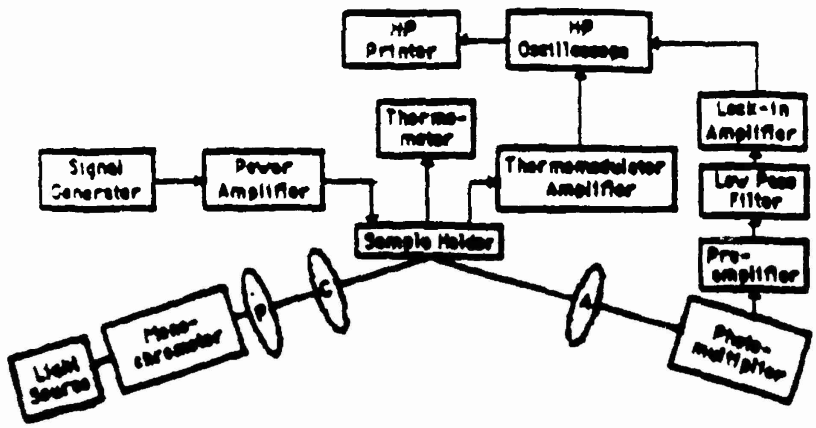

Figure 1. Schematic drawing of the exprimental equipment set up. P: polarizer, C: compensator, A: analyzer.

RESULTS AND DISCUSSION

The room temperature refractive index and absorption coefficients as a function of wavelength are shown in Fig. 2. The coefficients were measured using spectroscopic ellipsometry (11). The refractive index increased dramatically between 300 and 600 nm with a maximum value 3.7 near 600 nm (absorption edge), at higher wavelength it slowly decreased. Previous authors have reported for single crystal at romm temperature that the absorption edge was at 1.95 ev (635 nm) for polarized light E perpendicular to c axis, and 1.85 ev (670 nm) for polarized light E parallel to c axis (2). From this data it was decided to use a wavelength near 600 nm for the temperature sensitivity study because of the large refractive index and close to absorption edge.

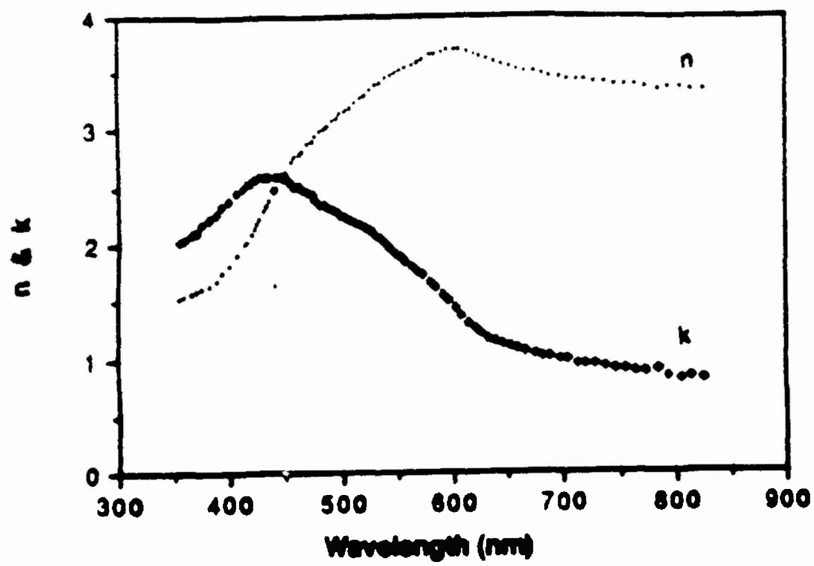

Figure 2. Refractive index (n) and absorption coefficient (k) of SbSI single crystal at room temperature as a function of wavelength.

Fig. 3 shows the change of the 633 and 580 nm reflectance coefficient with temperature modulation. The base temperature was between 5 and 35 ^{o}C with a 3.7 Hz ac modulation of approximately 0.02 ^{o}C. A sharp maximum in the change of the 633 nm reflectance coefficient was observed at 18.4 ^{o}C which is close to the reported transition temperature of SbSI. Similar results were obtained for the 580 nm reflectance coefficient, but the curve was shifted to higher temperature. This shift in the reflectance data is caused by the spontaneous polarization and the density of non-equilibrium electrons near the transition temperature. The phase transition in the ferroelectric semiconductor is also accompanied by anomalies in the temperature dependence of carrier concentration caused by a change in the donor activation energy near the Curie point, by changes in effective mass of the carriers and the concentration of donor centers (12). For wavelengths smaller than 580 nm and larger than 680 nm the temperature sensitivity of the reflectance coefficient was significantly smaller. Only in the wavelength region of the absorption edge was the temperature sensitivity large. The maximum sensitivity of photoconduction for single crystal SbSI was at 630-640 nm (13). The width of peak depends on experimental conditions.

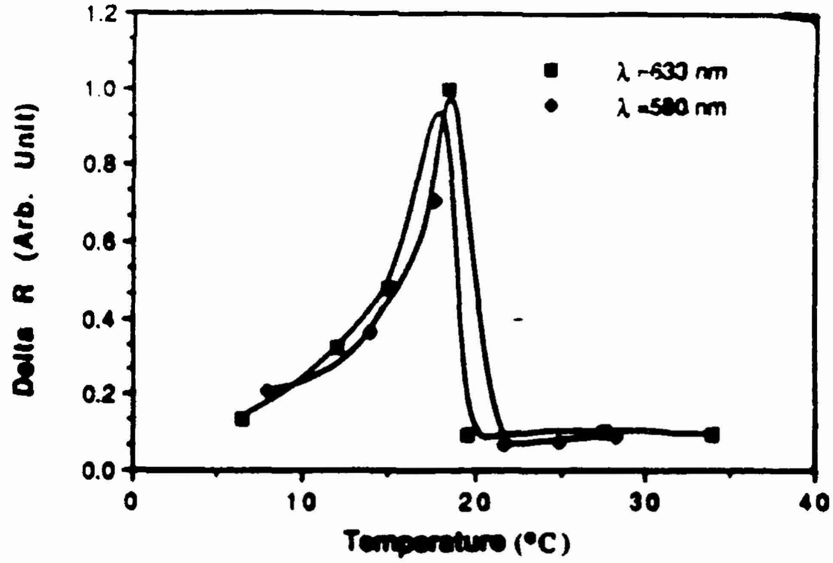

Figure 3. The change in the reflectance coefficient under a 3.7 Hz temperature modulation of 0.02 °C as a function of the base temperature.

Fig. 4 shows the dependence of the 580 nm reflectance coefficient at 15 °C on the magnitude of the temperature modulation. A linear dependence was found between 0.02 and 0.07 °C. Fig 5 (a) and 5 (b) show the 580 nm reflectance coefficient modulation and the corresponding temperature modulation respectively. It is obvious from Fig. 5 (a) that the reflectance coefficient is sensitive to much smaller variations in temperature than 0.02 °C as presently shown.The signal to noise ratio was 25 using a temperature modulation of 0.02 °C. This indicates that a temperature change of 10^{-3} °C can be detected using the pyro-optic properties of SbSI. Further increase in the sensitivity i.e. detection of a ΔT smaller than 10^{-3} °C, can be achieved by using the thinner samples and possibly thin films of SbSI.

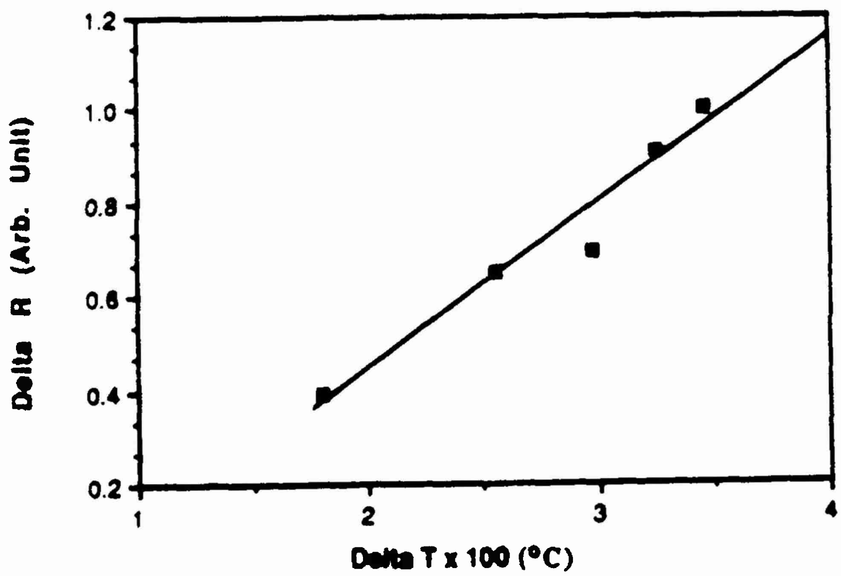

Figure 4. The dependence of the changing reflectance coefficient on the amplitude of the ac temperature modulation, at a base temperature of 15°C, a wavelength of 580 nm, and a frequency of 3.7 Hz.

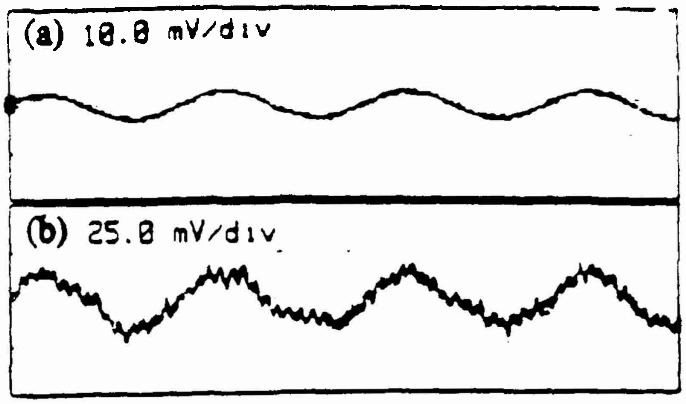

Figure 5. (a) Modulation of the reflectance coeffocient under a 3.7 Hz temperature modulation of 0.02 °C. (b) The temperature modulation.

CONCLUSION

Temperature variations of 10^{-2} °C have been measured in SbSI single crystal using null ellipsometry with thermoelectric sample mount. Considerations of the signal to noise ratio indicate that it is feasible to measure temperature variations smaller than 10^{-3} °C. The maximum temperature sensitivity has been found to occur at temperatures close to the ferroelectric phase transition (~20 °C) and at wavelengths close to the absorption edge.

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PATENT APPLICATION

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September 14, 1990

Thomas J. Monahan, Esq.
Patent Counsel & Manager
Intellectual Property Office
The Pennsylvania State University
306 West College Avenue
University Park, PA 16801

Re: Patent Application entitled:
"Pyro-Optic Detector and Imager"
Cross et al.
Your File: PSU 89-918
Our Ref.: 215-892570-NA

Dear Tom:

I am pleased to enclose the Notice of Allowability for the above-noted patent application. Unless I hear differently we will proceed to pay the Issue Fee in due course.

Before the Issue Fee is paid, I recommend that a review of the allowed claims be undertaken to assure that we have inserted no unnecessary limitations.

By copy of this letter to Drs. Cross and Bhalla, I ask them to review the attached allowed claims toward this end.

Sincerely,

PERMAN & GREEN

Dave

David N. Koffsky

DNK:jam
c: ✓Dr. L. Eric Cross
Dr. Amar S. Bhalla

L. E. Cross F. Ainger
A. Bhalla D. Damjanovic

PYRO-OPTIC DETECTOR AND IMAGER

FIELD OF THE INVENTION

This invention relates to a thermal imaging system and more particularly to a thermal imaging system which employs a pyro-optic detector whose refractive index is altered in accordance with local temperature variations therein.

BACKGROUND OF THE INVENTION

There are many types of infrared thermal imaging systems in the prior art. The most widely used classes of infrared imagers employ photon detection and thermal detection. In the latter category, i.e. thermal detectors, the pyro-electric effect present in certain materials is employed as the primary detection means. While the pyro-electric capabilities of materials are often very good, and can achieve a noise equivalent temperature differences of less than 0.01K, few detectors can approach that performance and still remain both commercially and practically usable. The main problems lie in electrical and thermal isolation of the sensor, electrical contacts to the readout, and the limiting of noise bandwidth which, together, all act to degrade the detector's response in an assembly or array of detectors.

As an example, many thermally detectors employ thin liquid crystals as the heat sensing medium. It is particularly difficult to temperature stabilize the liquid crystal media, as the electrical contacts thereto act as heat sinks and tend to dissipate the accumulated energy, thus decreasing the sensitivity of the system.

Others have attempted to avoid the heat dissipation problem by employing liquid crystal detection units in a light transmission arrangement. In specific, an infrared image is focussed on a liquid crystal detector which, in response to local temperature variations in the crystal medium, accordingly alters its local index of refraction. Subsequently, a polarized light beam is transmitted through the liquid crystal medium which interacts with the polarized light to locally alter the angle of polarization in accordance with the local changes in index of refraction. These changes are detected after the beam exits from the liquid crystal and enable the image to be reproduced. Transmission detection systems require reasonably thick liquid cells which exhibit both low thermal efficiency and significant crystalline noise. Such systems are described by B.F. Lamouroux et al. in "Signal-to-Noise Ratio Analysis of a Digital Polarimeter Application to Thermal Imaging", Review of Scientific Instruments, 54 (5), May 1983 pages 582-585; in "Infrared Video Camera at 10 Microns", Andre et al. Applied Optics Vol. 18, No. 15, August 1979 pages 2607-2608, and in British published patent application GB 2 150 387 A, to Elliot et al. entitled "Thermal Imager".

In U.S. Patent 4,160,907 to Bly, an infrared imager is described wherein a thin semiconducting film, such as

vitreous selenium is employed as the infrared detector. This detector exhibits a temperature-dependent optical absorption spectrum which results in local areas on the detector varying in transmissivity in relation to radiation incident thereon. Detection of the infrared radiation is accomplished by transmitting light through the detector and sensing, on the other side thereof, local changes in the intensity of the transmitted light as an indication of the infrared image. This systems suffers a decrease in sensitivity due to the loss of brightness which occurs as the result of having to sense the light, after its passage through the absorption medium.

Accordingly, it is an object of this invention to provide a pyro-optic detector wherein the use of electrical contacts to the pyro-optic element are avoided.

It is another object of this invention to provide a pyro-optic detector wherein the detection element exhibits high thermal efficiency.

It is still another object of this invention to provide a pyro-optic detector which employs a detection material exhibiting a high temperature coefficient of refractive index.

Yet another object of this invention is to provide a pyro-optic detector which avoids losses inherent in transmission imaging systems.

SUMMARY OF THE INVENTION

An infrared imaging system is described which includes a pyro-optic sensor for receiving a thermal image on one of its sides, the sensor exhibiting a substantial change in refractive index in responses to changes in its temperature. A light beam is projected onto a second side of the sensor, the beam being selectively, locally reflected by the sensor in accordance with local changes in its refractive index. A receiver detects the reflected beam and responds to the reflectance changes to derive a visible image of the thermal image.

The pyro-optic sensor comprises a sandwich structure which includes a film of energy absorbant material upon which the thermal image is received; a thin film of thermal-optic material; and a supporting layer which includes an optically transparent foam positioned next to the pyro-optic material on the side at which is directed an interrogating light beam.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a block diagram of a system embodying the invention;

Fig. 2 is a section view of the thermal optic detector;

Fig. 3 is a plot of changes in reflectance coefficient in an SbSI sample when it is temperature modulated.

DETAILED DESCRIPTION OF THE INVENTION

Referring to Fig. 1, an infrared scene 10 is imaged by lens 12 onto pyro-optic detector 14. A chopper 16 periodically interrupts the infrared scene, under control of chopper control 18. Pyro-optic detector 14 is housed within a constant temperature enclosure 20 whose sides 22 and 24 are transparent to electromagnetic radiation.

A light source 26 is directed via lens 28 through polarizing plate 30. The thus polarized light beam then impinges upon one side of pyro-optic detector 14, is reflected thereby and passes through phase plate 32 and polarization analyzer 34. The beam is then imaged by optical system 36 onto a charge coupled device (CCD) array 38, or any other device which is suitable for translating the photonic image into an electrical image. The pixel image from CCD array 38 is then fed via conductor 40 to microprocessor 42 which assembles the image for display. Microprocessor 42 also, via conductor 44, synchronizes the operation of chopper control 18. This synchronization enables microprocessor 42 to substractively process images to eliminate from the image both fixed pattern and time constant noise. This operation will be discussed in detail below. The output from microprocessor 42 is a video signal on line 46 which then may be viewed or further processed.

Referring now to Fig. 2, pyro-optic detector 14 is shown in section. Infrared image 10 is focussed onto an absorbing black layer 50. A pyro-optic film 52 is sandwiched immediately below and in intimate contact with

absorbing black layer 50 and has its temperature modified in accordance with temperature variations appearing on black layer 50 (as a result of the projection of infrared scene 10). An optically transparent, thermal isolating layer 54 supports pyro-optic film 52 and provides for the thermal isolation thereof. Layer 56 is an optically transparent glass, quartz or other material which is suitable for providing physical support and temperature isolation of pyro-optic film 52.

The interrogating, polarized light beam 60 from light source 26 (Fig. 1) impinges upon optically transparent layers 56 and 54 and is reflected by pyro-optic layer 52. It is the change in angle of polarization of light beam 60 resulting from this reflection which enables the thermal image on pyro-optic film 52 to be read.

Film 52 is preferably a material which can be formed as a thin film and exhibits large temperature coefficients of refractive index and birefringence. A variety of ferroic materials, ferroelectrics, ferroelastics and ferroelectric/ferroelastics meet this criteria. Table 1 below illustrates certain materials which exhibits a particularly large temperature coefficient of refractive index (n). It is seen from Table I that highly anisotropic materials posses high coefficients. For instance, antimony sulfur iodide and molybdenum disulfide are particularly useful in the temperature regions of $0^{\circ}C - 50^{\circ}C$. These materials along with certain organico naphtha and related substitutes are preferred materials for pyro-electric film 52.

TABLE 1

MATERIAL	TEMPERATURE RANGE (°C)	$\frac{d(n)}{dT}$ (1°C)
SbSI	0°C to 15°C	dn_c/dT = 7.5 X10^{-3}
	18°C	≥ 15 X10^{-3}
$BiVO_4$	20°C to 100°C	2.8 X$^{10-4}$
MoS_2	20°C to 50°C	dn/dT = 163 X10^{-4}
$PbTiO_3$	-60°C to -40°C	1.5 X10^{-4}
	-60°C to 0°C	(= 5150A) 1.6 X10^{-4}
$BaTiO_3$	20°C to 120°C	3.1 X10^{-4}
DSP	-40°C to 0°C	2.5 X10^{-5}
Fe -I Boracite	25°C to 70°C	3.3 X10^{-5}
Cu-Cl Boracite	80°C to 90°C	4.0 X10^{-5}
TGS	40°C to 300°C	3.3 X10^{-5}
SBN (61:39)	20°C to 80°C	4.5 X10^{-4}
PBZT	120°C to 130°C	5.0 x10^{-4}

Thermal isolating layer 54 is included to reduce thermal flow away from pyro-optic film 52. Aerogel, a critically dehydrated foam of silica is preferred for this purpose and is extremely effective in preventing convection losses while, at the same time, being transparent to optical radiation. Aerogel may be obtained from various suppliers or can be prepared in the laboratory (e.g., see "Ambient Temperature Supercritical Drying of Transparent Silica Aerogels", Tewari et al., Materials Letters, Vol. 3, Nos. 9, 10, pp. 363-367 (1985)).

In lieu of an aerogel film, other anodically deposited films on glass, which are thermally isolating, may also be substituted.

As shown in both Table I and Fig. 3, antimony sulfur iodide exhibits a substantial temperature coefficient of refractive index. Fig. 3 illustrates the alterations in the reflectance coefficient of an antimony sulfur iodide (SbSI) sample in accordance with a 0.02°C temperature modulation at 3.7 Hz. The optical properties of SbSI are known to be strongly coupled to its polar nature and the presence of a relatively high concentration of non-equilibrium electrons near the phase transition temperature. SbSI may also be deposited in extremely thin, continuous films. The Responsivity of an SbSI film (and all other thermal detecting films) can be expressed as follows:

$$R = \frac{Io}{(g^2 + w^2c^2t^2)^{1/2}}$$

For an idealized system with optimized optics and absorption of radiation where

I_o = energy contrast in thermal scene ($\sim 10^{-4}$ W cm^{-2})
g = thermal conductivity of pyro-optic
c = specific heat of pyro-optic
t = thickness of pyro-optic
w = 2 f (f = frequency)

As can be seen from the above relationship, assuming that an optimum pyro-optic material is chosen, its specific heat is fixed and varies very little across a diverse

range of materials. The most significant impact on Responsivity is made by reducing g and t. Thus by reducing the thickness of pyro-optic film 52 to a minimum, the responsivity of the system can be increased. The film's thermal conductivity is minimized by the placement of an aerogel layer 54 immediately below film 52. Aerogel exhibits a very low g - approximately 10^{-5} W/cm/K. Pyro-optic film thicknesses as low as 0.1 microns are preferred.

The operation of pyro-electric detector 14 in Fig. 2 results from localized temperature differences on pyro-optic film 52 causing localized changes in refractive index. When polarized light beam 60 impinges thereon, the beam's angle of polarization is rotated in accordance with the degree of change of the index of refraction at each of the local areas within film 52. It is to be noted that the optical interrogation system which converts the temperature differences to optical differences is an entirely <u>reflective</u> system and does not involve any passage of the interrogating beam through the pyro-optic material. Furthermore, the pyro-optic film 52, by virtue of its extreme thinness, enables substantial thermal sensitivity and attendant low thermal mass.

Referring now to Figs. 1 and 2 in conjunction, the operation of the invention will be described. As aforestated, an infrared scene 10 is imaged upon pyro-optic detector 14 causing localized changes in the temperature of pyro-optic film 52 and attendant localized changes in its index of refraction. Light beam 60, which is polarized in one direction by virtue of its passage

through polarizing plate 30, is reflected by pyro-optic film 52. As above stated, localized areas of beam 60 experience changes in angle of polarization in accordance with the localized changes in index of refraction. The reflected, interrogating beam 60 passes through phase plate 32 and orthogonally oriented polarizing analyzer 34. In the well known fashion, analyzer 34 passes only those areas of polarization which have been rotated from the othogonal polarization orientation. The scene is then imaged by optical system 36 onto CCD array 38 which is periodically read via line 40 into microprocessor 42. Within microprocessor 42 an image subtraction process takes place. The scene imaged on CCD detector 38 when chopper 16 obstructs the infrared scene is subtracted from the infrared scene which is viewed when chopper 16 does not obstructing the view. This enables the subtraction from the image of fixed pattern and transient noise. The thus processed image is then passed to a display via conductor 46.

As will be understood by those skilled in the art, the basic interrogation technique utilized herein is similar to ellipsometric methods. Phase plate 32 is employed to adjust the reflected beam at analyzer 34 so that a null occurs when pyro-optic detector 14 is at its nominal, non-imaging condition. Enclosure 20 is preferably temperature controlled to provide pyro-optic detector 14 with a constant ambient, which ambient does not differ significantly from the temperature range being detected. Light source 26 may either be an uncollimated light source or may be a source of collimated light (e.g. a laser) whose beam is scanned over the surface of pyro-optic detector 14. In such case, the scan rate of

light source 26 will be synchronized with the operation of microprocessor 42.

It should be understood that the foregoing description is only illustrative of the invention. Various alternatives and modifications can be devised by those skilled in the art without departing from the invention. Accordingly, the present invention is intended to embrace all such alternatives, modification and variances which fall within the scope of the appended claims.

CLAIMS

We Claim:

1. An infrared imaging system comprising:

pyro-optic sensing means for receiving a thermal image on a first side of said sensor means, said sensor means exhibiting a change in its refractive index in response to changes in its temperature;

means for directing an interrogating optical beam to a second side of said sensor means, said optical beam being reflected and selectively alerted by said sensor means in accordance with local changes in its refractive index; and

means for receiving said reflected beam and responding to said selective reflectance alterations to derive a visible image of said thermal image.

2. The imaging system of Claim 1 wherein said pyro-optic sensing means is a multilayer, planar sandwich structure comprising:

a thin film of pyro-optic material; and

a supporting layer transparent to said interrogating light beam.

3. The imaging system of Claim 2 wherein said pyro-optic material is selected from the group consisting

of SbSI, $BiVO_4$, MoS_2, $PbTiO_3$, DSP, Fe-I Boracite, Cu-Cl Boracite, TGS, SBN (61:39) and PBZT.

4. The imaging system of Claim 2 wherein said pyro-optic material is selected from the group consisting of SbSI and $BiVO_4$.

5. The imaging system of Claim 2 wherein said sandwich structure further comprises:

a film of energy absorbent material disposed on said pyro-optic material, for receiving said thermal image.

6. The imaging system of Claim 5 wherein said supporting layer comprises:

an optically transparent foam layer of low thermal conductivity, adjacent said thin film of pyro-optic material; and

a glassy layer for supporting said sandwich structure.

7. The imaging system of Claim 6 wherein said transparent silica foam layer is aerogel.

8. The imaging system of Claim 6 further comprising:

container means for enclosing said pyro-optic sensing means and maintaining it at a stable temperature.

9. The imaging system of Claim 2 wherein said directing means includes a first polarizer for polarizing said interrogating optical beam in a first direction.

10. The imaging system as recited in Claim 9 wherein said receiving means includes a second polarizer whose direction of polarization is orthogonal to said first direction after reflection of said optical beam, portions of said reflected beam exhibiting local rotated angles of polarization from said first direction depending upon said local changes in refractive index of said pyro-optic sensing means, whereby said local rotated reflected optical beam portions are subjected to lesser attenuation by said second polarizer than said nonrotated portions.

11. The imaging system of Claim 10 further comprising:

chopper means for periodically blocking the pyro-optic sensor means from receiving the thermal image; and

means in said receiving means for subtracting the image derived when said thermal image is blocked by said chopper means from a thermal image derived when said pyro-optic sensor means is not blocked by said chopper means;

whereby fixed pattern and system noise is cancelled from the image.

12. A pyro-optic sensor for use in an infrared imaging system having an interrogating optical beam, said sensor comprising:

a thin film of pyro-optic material having two major surfaces, said material reflective of said interrogating optical beam;

a glassy support plate;

a low thermal conductivity optically transparent foam disposed between a major surface of said film, and said glassy plate; and

a layer of infrared absorbent material disposed on another major surface of said film of pyro-optic material.

13. The sensor of claim 12 wherein said pyro-optic material is selected from the group consisting of SbSI and $BiVO_4$.

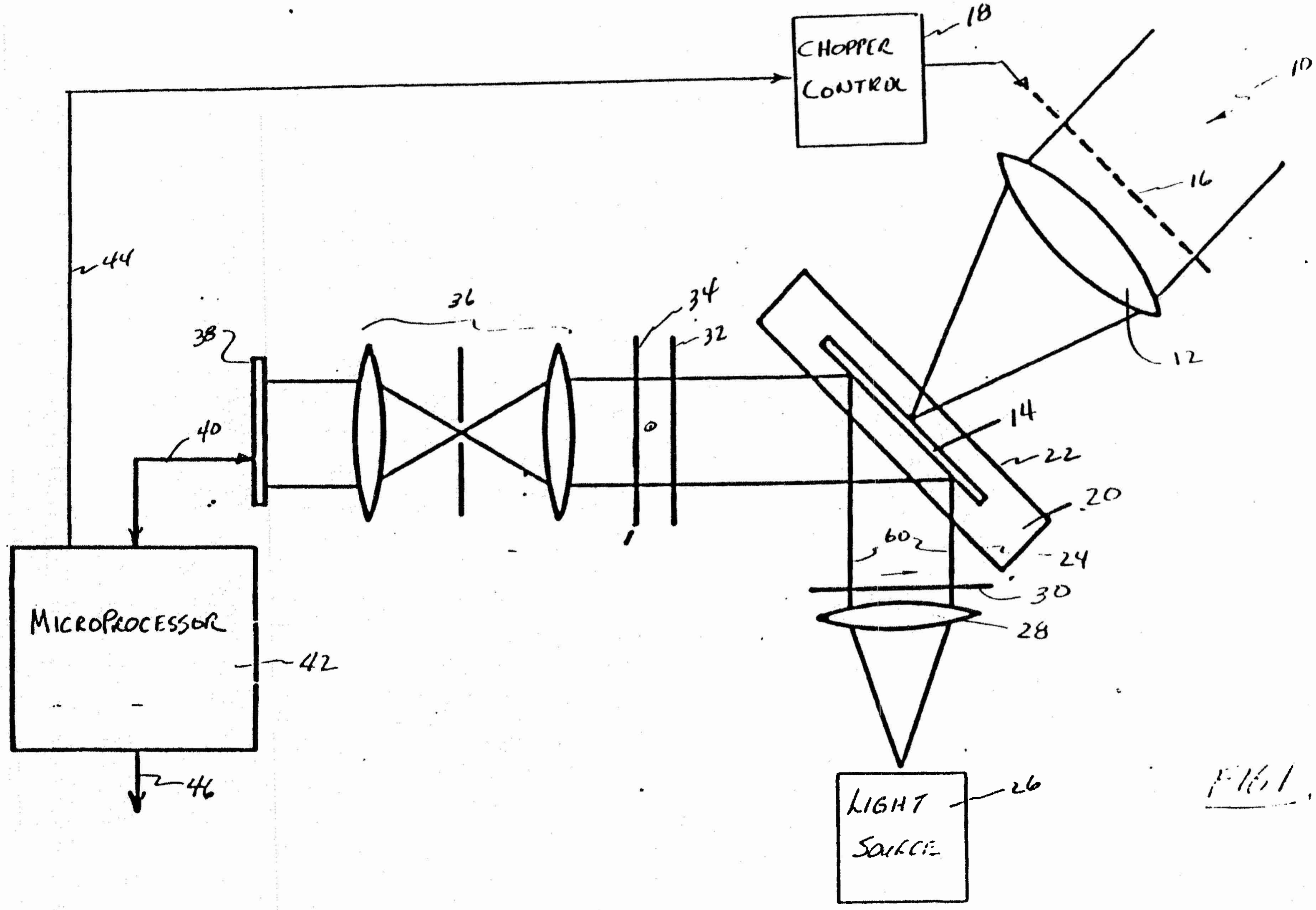
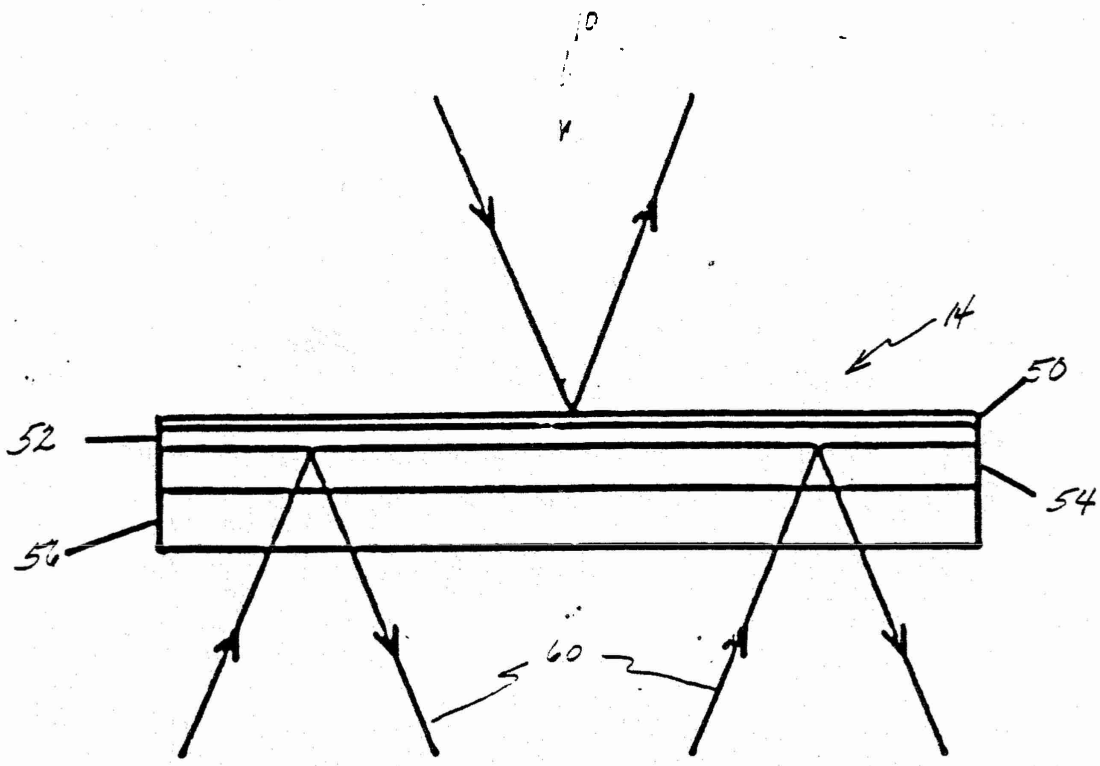
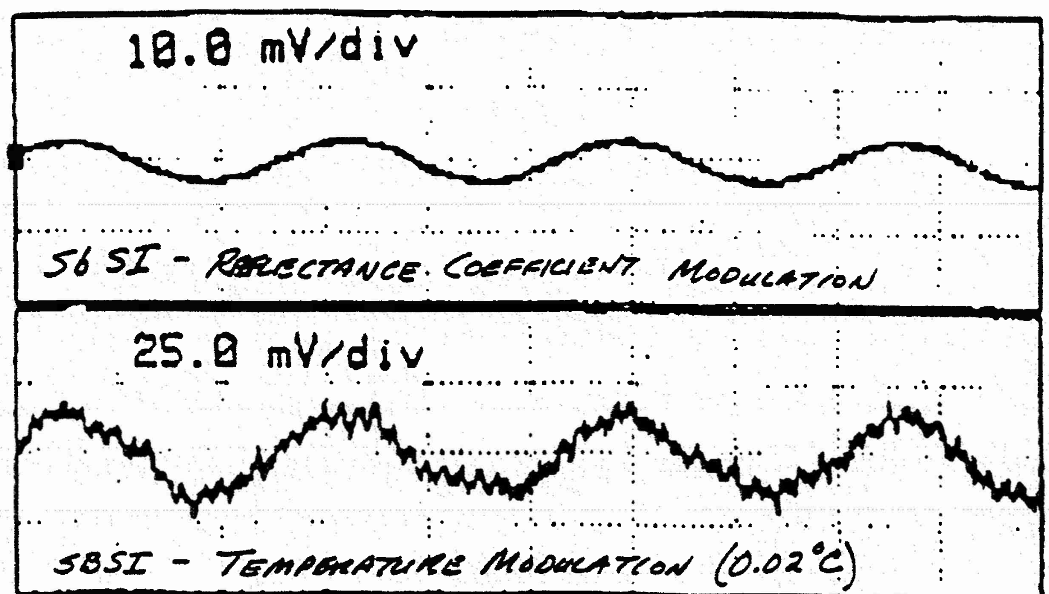

CHOPPER CONTROL
18
10
16
12
14
22
20
24
30
28
60
LIGHT SOURCE
26
MICROPROCESSOR
42
46
44
40
38
36
34
32

FIG 1



10
14
50
52
54
56
60

FIG 2



10.0 mV/div
56 SI - REFLECTANCE COEFFICIENT MODULATION
25.0 mV/div
58SI - TEMPERATURE MODULATION (0.02°C)

FIG 3